(12) UK Patent Application (19) GB (11) 2 361 245 (13) A

(43) Date of A Publication 17.10.2001

(21) Application No 0009393.0

(22) Date of Filing 14.04.2000

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(51) INT CL[7]
C23C 14/08 , C03C 17/245

(52) UK CL (Edition S)
C7F FBAX FPCX FQ908 FR908 F103 F109 F211 F302 F307 F782
U1S S2055 S3069

(56) Documents Cited
US 5630918 A US 5605610 A US 5603778 A
US 5116479 A US 4842705 A US 4690745 A
US 4345000 A
DE004000664 A1 & WPI Accession no 91-216066

(58) Field of Search
UK CL (Edition R) C7F FBAE FBAL FBAX FBBE FBBL FBBX FBXE FBXL FBXX FCSE FCSL FCSM FCSX FCVE FCVL FCVM FCVX FPCE FPCL FPCX FPDE FPDL FPDX
INT CL[7] C03C 17/23 17/245 , C23C 14/08
Online; WPI, EPODOC, JAPIO

(54) Abstract Title

High conductivity indium-tin-oxide films

(57) A transparent electrical conductor deposited upon a substrate (9) by RF sputtering and in one embodiment consisting of a plurality of layers (1-7) of Indium-Tin-Oxide in which alternate layers are oxygen enriched layers. Embodiments of the invention can be formed upon a substrate at low temperature (in the range 20 to 100°C) and the resistivity of the complete film has a relaxed dependency upon the oxygen concentration present in the deposition chamber during the formation of the oxygen enriched layers. The formation of these films is relatively simpler than methods requiring the introduction of hydrogen to the deposition chamber or the in situ measurement of the oxygen concentration during film growth. In this embodiment the film typically has a resistivity of $5\times10^{-4}\Omega$cm and a transparency of greater than 90%.

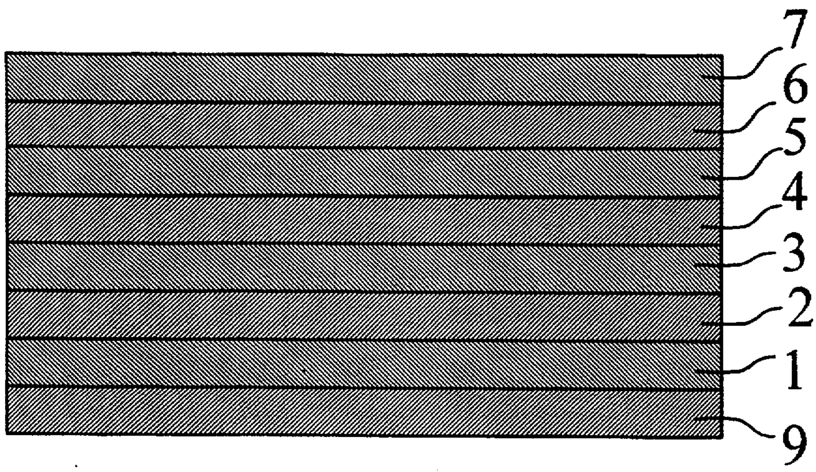

Figure 1

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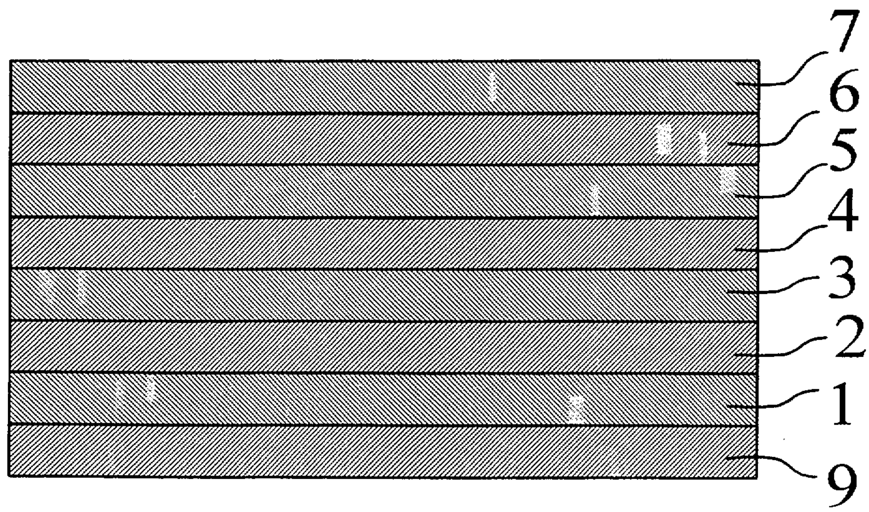

Figure 1

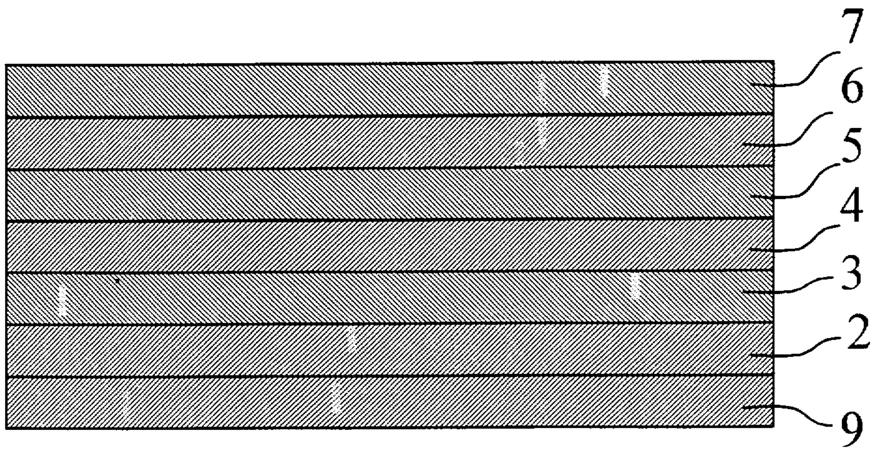

Figure 2

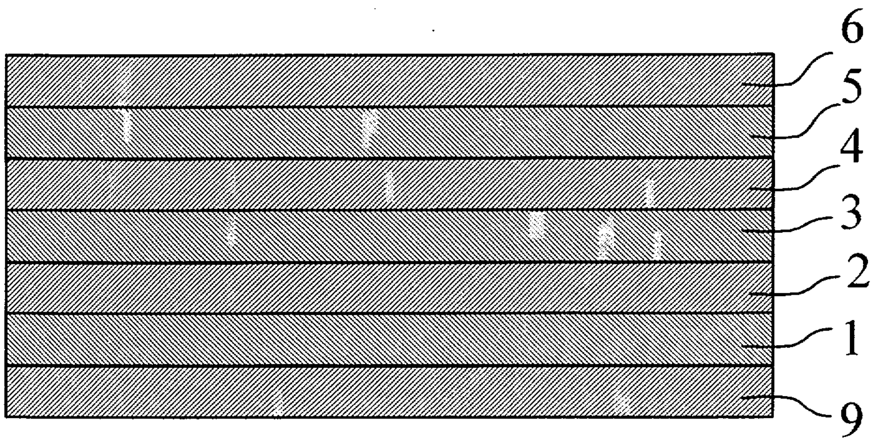

Figure 3

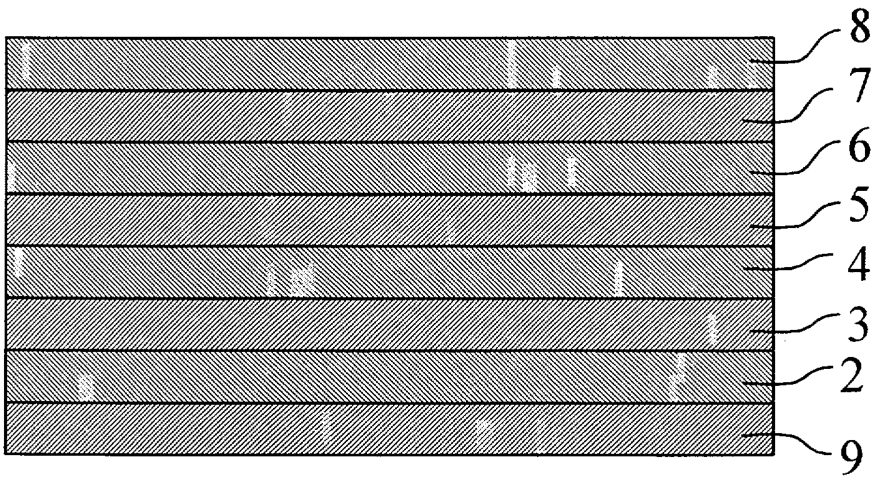

Figure 4

High Conductivity Indium-Tin-Oxide Films

This invention relates to optically transparent and electrically conductive films made of Indium-Tin-Oxide and deposited by the sputtering process.

Thin films of Indium-Tin-Oxide (ITO) can be produced that possess both the properties of optical transparency and electrical conductivity in the same film at the same time. ITO films find application in forming the electrodes to optoelectronic devices such as discrete light-emitting diodes (LEDs), liquid-crystal-displays (LCDs), organic LED displays and the like.

Prior to this invention it has been noted that for the production of low resistivity ITO films a closely controlled deposition-rate to oxygen-partial-pressure ratio has been required as set forth in Howson RP and Ridge MI, Thin Solid Films, 1981, 77, 119. Furthermore, for the production of low resistivity ITO films a low deposition-rate to oxygen-partial-pressure ratio has been required as set forth in Kawada A, Thin Solid Films, 1990, **191**, 297. Consequently in the production of ITO films with reproducible film quality using the prior art control of the oxygen concentration is critical and this has led to the requirement for elaborate and expensive methods of in situ monitoring of the oxygen concentration.

Another deficiency of the prior art is that low sheet resistance and high transparency can only be made to occur together when the film is deposited over a small range of oxygen partial pressures. This deficiency is exacerbated when the film is deposited onto a substrate with the substrate temperature below 100°C. There are many applications for ITO that involve the deposition of ITO onto plastic substrates or onto semiconductor devices which cannot be heated to high temperatures. It has been noted in "Semiconducting Transparent Thin Films", Hartnagel HL et al., IOP Publishing, Bristol and Philadelphia, 1995, that a deposition technique for producing ITO films with low resistivity and high transparency upon substrates at low substrate temperature which resulted in relaxed constraints upon the process parameters would be of considerable interest.

The introduction of hydrogen in the form of hydrogen gas or as water vapour to the gas mixture in the sputtering chamber has been observed to relax the constraints upon the process parameters, particularly when the ITO was deposited at low substrate temperature. Films with resistivities of 6×10^{-4} Ωcm were deposited with the substrate at room temperature as set forth in Ishibashi S et al., J. Vac. Sci. Technol., 1990, A8, 1399.

Objects of the present invention are, amongst others, to provide a technique for the deposition of ITO films with low resistivity, of the order of 5×10^{-4} Ωcm so that thin-films can be created that possess low sheet-resistance of the order of 50Ω/square and high-transparency of greater than 90%. Further objects of the present invention are that the films be deposited at low substrate temperature and that the required control of the oxygen concentration be sufficiently relaxed without introducing hydrogen into the sputtering chamber so that in situ monitoring of the oxygen concentration in the chamber during sputtering is not required.

According to the first aspect of the present invention there is provided an optically transparent electrical conductor deposited by RF sputtering with a multi-layer structure of typically, though not limited to, between seven and thirteen layers inclusive of ITO in which alternate layers are oxygen enriched layers.

The first aspect of the present invention also provides a method of enriching the oxygen enriched layers whereby the oxygen is introduced into the layer during the deposition of the layer by the introduction of oxygen gas into the sputtering chamber.

According to the second aspect of the present invention there is provided a method of preparing ITO films by the technique of RF sputtering whereby the properties of the film are insensitive to the exact concentration of oxygen in the chamber over the range 1% to 5% by mass during the deposition of the oxygen enriched layers.

According to the third aspect of the present invention there is provided a method of preparing ITO films by the technique of RF sputtering whereby the films are prepared with the substrate at low temperature, typically in, though not limited to, the temperature range 20 to 100°C.

Figure 1 is a section through a complete film in accordance with the first embodiment of the present invention.

Figure 2 is a section through a complete film in accordance with the second embodiment of the present invention.

Figure 3 is a section through a complete film in accordance with the third embodiment of the present invention.

Figure 4 is a section through a complete film in accordance with the fourth embodiment of the present invention.

A first embodiment of the invention will now be described by way of example with reference to Figure 1.

Films are deposited by sputtering sequential layers from an ITO target of composition 90% indium oxide (In_2O_3), 10% tin oxide (SnO_2) and of purity 99.99%, in an RF excited plasma in argon gas or in an RF excited plasma in a mixture of argon gas and oxygen gas.

Referring to Figure 1 the film is formed upon a suitable substrate 9, for example but not limited to, glass. Prior to starting the deposition process the chamber is evacuated to a pressure of approximately 2×10^{-6} torr. Argon gas is then admitted into the chamber to a pressure in the range 5×10^{-3} to 1×10^{-2} torr. A plasma is struck in the chamber, excited by an RF source with a power of typically though not limited to 200W for a 100mm diameter target. The film is deposited in sequential layers without breaking the vacuum.

Layer 1 is deposited by sputtering in the argon plasma. The layer is deposited to a thickness of typically though not limited to 17nm. After layer 1 has been deposited the substrate shutter is positioned to prevent further deposition upon the substrate. Oxygen is then admitted into the chamber to a ratio of oxygen to argon of typically though not limited to the range of 1:99 to 5:95 by mass. The substrate shutter is then removed to allow the deposition to continue with layer 2. Layer 2 is deposited to a thickness of typically though not limited to 17nm. After layer 2 has been deposited the substrate shutter is positioned to prevent further deposition upon the substrate. The oxygen supply is then cut off and the chamber continually pumped to reduce the concentration of oxygen to below 0.1%. The substrate shutter is then removed to allow the deposition to continue with layer 3. Layer 3 is deposited to a thickness of typically though not limited to 17nm. After layer 3 has been deposited the substrate shutter is then positioned to prevent further deposition upon the substrate. The oxygen supply to the chamber is restored and the oxygen concentration allowed to return to typically though not limited to 1% to 5%. The substrate shutter is then removed to allow the deposition to continue with layer 5, a second layer of oxygen enriched ITO. This sequence of operations resulting in the deposition of alternate oxygen enriched / non-oxygen enriched layers is repeated until the desired number of layers has been deposited. In this first embodiment the desired number of layers is seven and consequently the last layer deposited, layer 7, is deposited with the supply of oxygen to the chamber cut off.

In a second embodiment, referring to Figure 2, the procedure for the formation of the film is identical to the first embodiment except that the first layer deposited, layer 2, is deposited with the oxygen concentration in the sputtering chamber in the range typically 1% to 5%. Subsequent layers deposited alternate between oxygen enriched and non-oxygen enriched until the film is built up. The number of layers in this embodiment is an even number and the last layer is therefore not oxygen enriched.

In a third embodiment, referring to Figure 3, the procedure for the formation of the film is identical to the first embodiment except that the formation of the film is terminated with layer 6; a layer deposited with the oxygen concentration in the sputtering chamber in the range typically 1% to 5%. The number of layers in this embodiment is an even number.

In a forth embodiment, referring to Figure 4, the procedure for the formation of the film is identical to the first embodiment except that the first layer deposited, layer 2, is deposited with the oxygen concentration in the sputtering chamber in the range typically 1% to 5%, and the formation of the film is terminated with layer 8; a layer deposited with the oxygen concentration in the sputtering chamber in the range typically 1% to 5%. The number of layers in this embodiment is an odd number.

Obviously, many modifications and variations of the present invention are possible now that the present invention has been disclosed. Therefore, it is to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described above.

Claims

1. An optically transparent electrical conductor deposited by RF sputtering with a multi-layer structure of typically, though not limited to, between seven and thirteen layers inclusive of Indium-Tin Oxide (ITO) in which alternate layers are oxygen enriched.

2. The transparent electrical conductor according to Claim 1 wherein said conductor comprises of an electrically conductive material formed on a substrate.

3. The transparent electrical conductor according to Claim 1 wherein said conductor comprises of a plurality of ITO layers with alternate layers enriched with oxygen.

4. The transparent electrical conductor according to Claim 3 wherein each of the layers is approximately 17nm thick.

5. The transparent electrical conductor according to Claim 3 wherein the total number of layers is between seven and thirteen inclusive.

6. The transparent electrical conductor according to Claim 3 where the sheet resistance of the film is below 50Ω per square and the transmittance of the film is greater than 90% over the visible and near infra red range.

7. A method of fabricating ITO films by deposition upon a substrate.

8. A method of fabricating ITO films according to Claim 7 where the deposit consists of a plurality of layers deposited without breaking the vacuum.

9. A method of fabricating ITO films according to Claim 7 whereby the method of deposition is RF sputtering.

10. A method of fabricating ITO films according to Claim 9 whereby the sputtering is via an RF excited plasma in argon gas or whereby the sputtering is via an RF excited plasma in a mixture of argon gas and oxygen gas.

11. A method of fabricating ITO films according to Claim 10 wherein the oxygen enrichment is introduced into the oxygen enriched layers from oxygen in the plasma during the deposition of the layer.

12. A method of fabricating ITO films according to Claim 7 whereby the ITO is sputtered from an ITO target of composition 90% indium oxide (In_2O_3), 10% tin oxide (SnO_2) and of purity 99.99%.

13. A method of fabricating ITO films according to Claim 10 in which the oxygen gas as a percentage of the total gas mixture is in the range 1% to 5% by mass.

14. A method of fabricating ITO films according to Claim 7 whereby the substrate temperature during deposition is in the approximate range 20 to 100°C.

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Application No:	GB 0009393.0	**Examiner:**	Pete Beddoe
Claims searched:	1-14	**Date of search:**	14 August 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C7F (FBAE, FBAL, FBAX, FBBE, FBBL, FBBX, FBXE, FBXL, FBXX, FCSE, FCSL, FCSM, FCSX, FCVE, FCVL, FCVM, FCVX, FPCE, FPCE, FPCL, FPCX, FPDE, FPDL, FPDX)

Int Cl (Ed.7): C23C 14/08; CO3C 917/23, 17/245)

Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	US 5630918	(TOSOH) see esp exs	7-11 at least
X	US 5605610	(ANELVA) see esp col6 lines 50-67	7-11 at least
X	US 5603778	(CANON) see esp col9 lines 38-45	7-11 at least
X	US 5116479	(NIHON) see esp exs	7-11 at least
X	US 4842705	(MUELLER) see esp col2 line 52 - col3 line 3	1,7 at least
X	US 4690745	(MERCK) see esp col3 line 53 - col4 line 9	7-11 at least
X	US 4345000	(NITTO) see esp exs	7-11 at least
X	DE 4000664 A1 & WPI Accession no 91-216066 (SIEMENS) see cols 1-2 & English abstract		1-7

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.